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PROGRESS REPORT

OFFICE OF NAVAL RESEARCH  
Contract Nonr-1129(00)  
Project NR 036-012

Period Covered:  
February 1 through  
July 31, 1954

Institute of Polymer Research  
Polytechnic Institute of Brooklyn  
99 Livingston Street  
Brooklyn 1, New York

August, 1954

POLYTECHNIC INSTITUTE OF BROOKLYN

OFFICE OF NAVAL RESEARCH CONTRACT Nonr-1129(00)

Project NR 036-012

February 1 to July 31, 1954

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PROGRESS REPORT

ABSTRACT

Further experimental results on the adsorption of polyvinyl acetate and on polyvinyl butyral have been obtained. The amounts adsorbed are functions of the molecular weight, but these functions vary greatly with the solvent, running inversely with the solvent power.

The amounts adsorbed are a rather weak function of the temperature, again depending on the solvent.

The amounts adsorbed and temperature and solvent dependency vary with the origin of the polyvinyl acetate. This may be due to different degrees of branching.

With respect to the reactions of the wash primer constituents, the hydroxyl groups of the butyral resin are essential for the complexing with  $\text{Cr}^{3+}$  and other ions. On precipitation in the presence of water all the chromium can be separated from the resin by strong chelating agents, but only about three-fourths of the resin can be separated from the chromium phosphate by organic solvents, the remainder of the complex being most difficult to break by this method.

Viscosity and electrophoretic experiments indicate that, while in solution, the chromium ions attached to the

resin endow the latter with the properties of a polyelectrolyte, with phosphate as the counter ions.

A detailed discussion of the general function of the resin in the wash primer, and as an assistant for corrosion protection, is put forward tentatively on the basis of the available information.

August, 1954

POLYTECHNIC INSTITUTE OF BROOKLYN

OFFICE OF NAVAL RESEARCH CONTRACT Nonr-1129(00)  
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PROGRESS REPORT

INTRODUCTION.

As in the past, our work aimed at the elucidation of the part played by the polymer-resin constituent of the Vybond Process, and related wash primer actions. In particular, we aim at providing an insight into the effect of resin structure, into the changes occurring in the latter during the formation and application of the wash primer, and into the reactions which permit the resin to perform as observed.

In pursuit of this we sub-divided our investigation into the following phases: (a) characterization of parent polyvinyl acetates (PVAc) used for the polyvinyl butyral (PVB) preparation; (b) characterization of the PVB and comparison with the parent polymer; (c) characterization of the PVB recovered from the wash primer; (d) study of the reactions in which the resin participates; (e) study of the adsorption of PVAc, PVB, and related resins on solid surfaces, before and after the Vybond or wash primer process.

In previous phases of work under this contract, progress was made in divisions (a), (b), (d) and (e). Further progress within these lines will be reported below, together with some work in division (c) preceding the preparation of recovered resin. However, inasmuch as these divisions are somewhat artificial and serve mainly to illustrate the general objectives, it has been often found preferable in the presentation of the experimental material to cut across their lines.

#### EXPERIMENTAL AND RESULTS.

##### I. Preparation and Characterization of Polyvinyl Acetate.

In a previous report a method has been described using photoinitiation and bis-azo-isobutyronitrile as catalyst, by which high molecular weight samples of polyvinyl acetate had been prepared for adsorption measurements. This sample was used to extend the molecular range of our adsorption studies beyond the narrow limits of the commercial samples XYSG and XYHL. In order to make sure that any differences between the commercial and laboratory samples were due to molecular weight and not to the method of preparation, additional lower molecular weight samples were prepared by photoinitiation employing high concentration of the same catalyst. Determining molecular weights by light scattering, polyvinyl acetate sample PVAc-2 was found to have a weight average molecular weight of 993,000 (catalyst to monomer ratio of  $1:4.65 \times 10^4$ ) while polymer samples PVAc-4



and PVAc-6 showed weight average molecular weights of 527,000 and 337,000 respectively (catalyst to monomer ratios of  $1:6.2 \times 10^2$  and  $1:86.3$ ).

These three samples and the two commercial samples PVAc-XYSG and PVAc-XYHL span a molecular weight range of more than 6-fold. They were further characterized by viscosity measurements in methyl ethyl ketone at 25°C. The results are given in Table I. (Part of this table has been reported previously).

T A B L E I

Polymer Designation	% Conversion	$[\eta] \frac{\text{ml}}{\text{gm}}$	$k'$	$\overline{M}_w \times 10^3$	$(\overline{R}^2)^{1/2}$
PVAc-2	12%	275	.54	993	460 Å
PVAc-4	14.5	160	.35	527	386 Å
PVAc-6	15.0	108	.69	337	264 Å
PVAc-XYSG	High	80.5	--	264	204 Å
PVAc-XYHL	"	50.7	--	155	188 Å

## II. Adsorption of Polyvinyl Acetates.

The experiments reported in this section fall into two groups. The first set of results refers to experiments which were conducted directly under the auspices of this project. The polymers referred to are those listed in Table I above. The analyses for polyvinyl acetates in solution were carried through (1) by infra-red adsorption. An adsorption peak of 5.73 microns characteristic of the carbonyl group in polyvinyl acetates was

used.

The second set of experiments on the adsorption of polyvinyl acetates was conducted by a graduate student at the Polytechnic Institute of Brooklyn, whose experimental program was arranged to complement the contract work. This research was begun before the infra-red analytical techniques were developed, so that viscosity measurements were used to determine concentration changes. The possibility of fractionation on adsorption renders the quantitative aspect of these experiments somewhat open to question, but should not invalidate the general conclusions.

1. The adsorption of polyvinyl acetate from carbon tetrachloride solution on iron powder at 30.4°C. was measured as a function of concentration. The samples used are the polymers characterized in Table I. The isotherms obtained are presented in Fig. 1. The equilibrium adsorption values corresponding to the flat portion of the isotherms are listed in Table II. The iron powder was manufactured by the carbonyl process as previously reported.

T A B L E    II

<u>Sample</u>	<u><math>\bar{M}_w \times 10^3</math></u>	<u>Equilibrium adsorption mg/gr. Fe powder</u>
PVAc-2	993	2.64
PVAc-4	527	2.18
PVAc-6	337	1.80
PVAc-XYSG	264	1.55
PVAc-XYHL	155	1.47

The intrinsic viscosity of polyvinyl acetate XYSG in carbon tetrachloride is 33. This is very low as compared with the value of 80.5 in methyl ethyl ketone reported in Table I. Since intrinsic viscosity increases with increasing solvent power, it is evident that carbon tetrachloride is a very poor solvent. In order to determine how adsorption depended on solvent power, methyl ethyl ketone (MEK) as good solvent had been tried but discarded, because the carbonyl group interferes with the infra-red analysis for polyvinyl acetate. After further search, we found 1,2-dichloroethane as suitable for our work. There, the intrinsic viscosity of XYSG is 110, indicating a good solvent; the analysis by infra-red could also be easily conducted. Calibration data on optical density at 5.73  $\mu$  versus concentration for XYSG is given in Table III and Fig. 2. The adsorption obeys Beer's law.

T A B L E III

<u>Concen. gr. polymer/ 100 mm. solution</u>	<u>Optical Density (5.73 <math>\mu</math>)</u>
0.0119	.068
0.0298	.165
0.0596	.326
0.0745	.405
0.1489	.796
0.2100	1.063

Four adsorption isotherms on carbonyl-iron powder were so far determined in 1,2-dichloroethane as solvent. The

results are listed in Table IV and the adsorption isotherms are shown in Figs. 3 and 4.

T A B L E IV

<u>Polymer Designation</u>	<u>Temperature</u>	<u>Amount Polymer Absorbed mg/gr Fe</u>
PVAc-2	30.4°C.	.605
PVAc-2	51.0°C.	.618
PVAc-XYSG	30.4°C.	.530
PVAc-XYHL	51.0°C.	.529

Our results up to this point seem to illustrate that:

- (a) the amount of adsorption increases with molecular weight in the good solvent, as well as in the poor solvent;
- (b) the amount of adsorption is a less sensitive function of molecular weight in the good solvent than in the poor solvent.
- (c) there is a slight increase in equilibrium adsorption with increasing temperature.

Some experiments were carried out varying the temperature in  $\text{CCl}_4$  solutions. The results are the same as in 1,2-dichloroethane. A slight increase in adsorption occurs with an increase in temperature. The results are listed in Table V. The isotherms are plotted in Fig. 5.

T A B L E V

<u>Polymer Designation</u>	<u>Temperature</u>	<u>mg adsorbed/gr Fe</u>
PVAc-XYSG	30.4°C	1.55
PVAc-XYSG	48.5°C.	1.62

Finally, some experiments were carried out using benzene as a solvent. Here, the results differ from those in 1,2-dichloroethane and  $\text{CCl}_4$ . Only a slight change in adsorption occurs as a function of the molecular weight of the polymer. These results are listed in Table VI.

T A B L E VI

<u>Polymer Designation</u>	<u>Temperature</u>	<u>mg.polymer/gr Fe.</u>	<u>[<math>\eta</math>] in benzene</u>
PVAc-2 (993,000)	30.4°C.	0.695	---
PVAc-XYSG (275,000)	30.4°C.	0.680	93.0

Several experiments were carried out using Alcoa Activated Alumina as adsorbent. These experiments yield interesting results, but also show that activated alumina is not a suitable adsorbent for our purposes. For once, equilibrium is reached very slowly. After 7 hours, e.g., of continuous shaking, equilibrium had not been attained, whereas equilibrium is obtained within one hour if iron powder is used as adsorbent. A typical run is reproduced in Table VII.

T A B L E VII

PVAc-XYNL; 1,2-dichloroethane - 30.4°C.

<u>Original Conc.</u>	<u>Final Conc.</u>	<u>Time Shaking.</u>	<u>mg./gr.</u>
0.2224	0.0970	30 minutes	2.51
0.2224	0.845	1 hour	2.76
0.2224	0.595	2 hours	3.26
0.2224	0.0510	4 hours	3.43
0.2224	0.0395	7 hours	3.66

A second effect exhibited by adsorption measurements with samples XYSG and PVAc-2 on aluminum oxide shows the adsorption of PVAc-2 to be much lower than that of XYSG. The data in Table VIII were taken at 30.4°C. after shaking for 3 hours. The initial solution concentrations were approximately 0.2%.

T A B L E VIII

<u>Polymer Designation</u>	<u>mg adsorbed/gr. Al<sub>2</sub>O<sub>3</sub></u>	<u>Solvent</u>
PVAc-XYSG (275,000)	2.37	1,2-dichloroethane
PVAc-2 (990,000)	0.64	1,2-dichloroethane

These observations may be explained by a large internal surface of alumina which is partially blocked to the polymer by the irregular configuration of the individual alumina particles. In order to reach these surfaces the polymer molecular must slowly diffuse through the crevices; this will be easier for polymers of low than high molecular weights, so that the equilibrium adsorption may become a different function of molecular size, other than the molecular weight effect in free adsorption.

2. The second set of adsorption experiments was conducted on three polyvinyl acetate samples supplied by the du Pont Co. These will be referred to as samples A, B, and C. Using a relationship between osmotic molecular weights and viscosity in acetone obtained by Houwink, <sup>(2)</sup>  $[\eta] = 1.76 \times 10^{-4} M^{0.68}$ , the molecular weights were established as given in Table IX.

The adsorbents used in these experiments were reagent grade sea sand which was purified by washing with hydrochloric

T A B L E IX

<u>Sample</u>	<u>[<math>\eta</math>]</u>	<u><math>\overline{M}_n \times 10^3</math></u>
A	54.8	137.4
B	118.6	430.5
C	308	1,738.0

acid, and reagent grade iron powder which was washed with acetone and dried under vacuum. The surface area of these materials was determined by examination under a microscope, that of the sea sand was 139 cm<sup>2</sup>/gm, and of the iron 159 cm<sup>2</sup>/gm. The following are the results which should be compared with those under (1) above.

a. The adsorption isotherms of samples A, B, and C on silica from a toluene solution at 25°C. is shown in Fig. 6. The influence of molecular weight upon adsorption is striking.

The adsorption isotherms of samples A and B on iron powder from toluene at 25°C. is plotted in Fig. 7. The same general molecular weight relationship is preserved, though a slight increase in quantity with respect to the results of Fig. 6 can be noted.

b. The adsorption of samples B and C on silica from methyl ethyl ketone (MEK) solution is plotted in Fig. 8. Much less is adsorbed than from toluene solution as can be seen from comparison with Fig. 6. The viscosity of the polymers is higher in MEK than in toluene, i.e., MEK is the better solvent. The results are listed in Table X. Measurements are at 25°C.

T A B L E X

<u>Sample</u>	<u><math>[\eta]</math> in toluene</u>	<u><math>[\eta]</math> in methyl ethyl ketone</u>
A	39.0	
B	80.0	108.0
C	178.0	274.0

g. The adsorption of polymer C on silica from MEK decreased on increase in temperature. The results are plotted in Fig. 9.

The adsorption of polymer C from toluene on to silica also decreases with increasing temperature, see Fig. 10.

Assuming that the areas of sea sand and iron powder as observed by examination under the microscope are the true surfaces available to the polymer molecule, we find first that the difference due to the nature of the surface is small in this case. We find further that the area per adsorbed molecule is always small, so that the polymer layer must be several hundred angstroms thick. It has been shown by other workers<sup>(3)</sup> that adsorbed polymer does penetrate a considerable distance into the solution, but the values we can calculate from the data here appear to be on the large side. A correction may have to be applied due to the fact that minor crevices in the adsorbent particles available to the polymer molecule are not visible under the microscope. This would cause an underestimation of the surface area and an overestimation of the amount adsorbed per unit area.



### III. Adsorption of Polyvinyl Butyral.

A series of experiments on the adsorption of polyvinyl butyrals XYHL and XYSG has been started. The adsorbent used is iron powder. Since infra-red adsorption was such a sensitive analytical tool for the determination of polyvinyl acetate, the same method was tried here too.

After a number of preliminary experiments, it was found that an adsorption peak at 9.06 microns corresponding to the OH-group was suitable for the analysis of the butyrals in ethylene dichloride at concentrations of less than .25%. The adsorption obeyed Beer's law. The peak was not as sensitive to concentration as that used for the polyvinyl acetate experiments and the accuracy of the results for the butyrals is correspondingly lower. The calibration curve is the same for XYHL and XYSG and is given in Fig. 11.

Experiments were conducted to determine the length of time the polymer should be shaken with the iron powder to ensure saturation. The results are shown in Fig. 12. Three hours was established as a safe shaking time for future experiments.

The solutions of XYHL and XYSG were shaken at 30°C. and 50°C. 20 ml. of solution and 15 gm. of iron powder were used in every experiment. The results are given in Fig. 13. and are preliminary. An increase in adsorption over polyvinyl acetate under comparable conditions is noted.

IV. Wash Primer Formation.

Further series of experiments were conducted on the chromium phosphate wash primer itself. This solution was prepared from the mixture of three solutions, and a final addition of butyl alcohol, as indicated below. Polyvinyl butyral sample XYHL was used throughout.

<u>Solution</u>	<u>Components</u>	<u>Parts by weight</u>	
A-33 <sup>1</sup> / <sub>3</sub> % aq CrO <sub>3</sub>	CrO <sub>3</sub>	.465	
	water	<u>.930</u>	
			1.40
B - 10% H <sub>3</sub> PO <sub>4</sub> in acetone	85% H <sub>3</sub> PO <sub>4</sub>	1.095	
	Acetone	<u>9.865</u>	10.95
C - 15% PVB in ethanol	Polyvinyl butyral	10.95	
	ethanol (95%)	<u>62.20</u>	
			73.15
	n-butanol		<u>14.50</u>
			100.00
			=====

A is added to B and this mixture is added to C dropwise with mechanical stirring at 45°C. The charge is maintained at 45°C. for 25 minutes under stirring. In all experiments to follow, the wash primer was aged for at least one day.

1. The chromium phosphate wash primer was precipitated

in an excess of water, the precipitate, a green, rubbery material, separated and repeatedly washed with water. No chromium was detected in any of the wash liquids. When thoroughly washed, the precipitate becomes resinous. Quantities of this precipitate (Cr-PVB-WP) were treated in aqueous solutions of three chelating agents: a. Oxalic acid; b. Ethylene diamine; c. Ammonia triacetic acid,  $N(CH_2COOH)_3$ . All three reacted with the precipitate removing part or all of the chromium.

The experimental details were as follows: Cr-PVB-WP samples were placed in .6 molar oxalic acid, or in .6 molar ethylenediamine. The complexing agent was present in ca. 300-fold excess, and the reaction allowed to proceed at  $85^\circ C. \pm 2^\circ$  for 4 hours.

In oxalic acid the Cr-PVB-WP took on a blue tinge in 25 minutes. In 50 minutes the supernatant solution was noticeably green and the polymer appeared lighter green, the blue having disappeared. From here on the green was leached off the polymer until in about 90 minutes the polymer was white. The remaining white polymer is insoluble in MEK. If the wash primer is complexed with oxalic acid at room temperature, the action is much slower. Most of the color is removed from the polymer in a few days, but the residual polymer has a light blue-green color even after standing on contact with oxalic acid solution for several weeks.

The ethylene diamine solution reacted with the wash

primer precipitate turning it purple in color. A very small amount of chromium was leached from the polymer.

Only qualitative experiments were conducted with ammonia triacetic acid. This was an effective complexing agent and removed much of the chromium from the polymer. We were not able, though, to remove all the chromium from the precipitate as was possible with oxalic acid.

A series of three control experiments were run in parallel with the above. Blank wash primer solution without resin, with polyvinyl acetate substituted for polyvinyl butyral, and with acetylated polyvinyl butyral instead of XYHL were prepared. The polyvinyl acetate sample used was the same parent material employed in the manufacture of XYHL polyvinyl butyral. The acetylated polyvinyl butyral was prepared by refluxing XYHL resin for four hours with 25 ml. of a solution of 12% by volume of acetic anhydride in pyridine for each gram of polyvinyl butyral. By this procedure most of the free hydroxyl groups remaining on the polymer may be presumed acetylated.

For the purpose of further discussion the following additional abbreviations will be used:

PVP-WP -- the normal chromium phosphate wash primer.

PVAc-WP -- wash primer with polyvinyl acetate substituted for polyvinyl butyral.

PVBAc-WP -- the acetylated butyral wash primer.

B1 -- the solution blank without resin.

The PVB-WP is a clear, viscous, dark green solution. B1 contained a  $\text{CrPO}_4$  sediment, as did PVAc-WP and PVBAc-WP. In the case of the latter two, it was not clear whether or not resin was bound to the  $\text{CrPO}_4$  sediment. On precipitating these controls in an excess of water, B1 yielded a powdery precipitate of  $\text{CrPO}_4$ , PVAc-WP and PVBAc-WP yielded green resins similar in appearance to Cr-PVB-WP, but rather more rubbery than the latter precipitate.

The  $\text{CrPO}_4$  precipitate from B1 was easily complexed with oxalic acid yielding a blue-green solution, and with ethylene diamine yielding a violet solution. The PVBAc and PVAc wash primers precipitates behaved in the same manner with the complexing agent as those of the PVB-WP. Complexing with ethylene diamine colors the PVAc and PVBAc precipitates purple, but dissolves little chromium.

2. Solubility experiments on the PVB wash primer precipitates were conducted together with the PVAc-WP and PVBAc-WP and B1 control precipitates. They were placed in 100 times their weight of solvent. Solvents used were dioxane, MEK, dimethyl formamide (DMF), and 95% ethanol (EtOH).

In these solvents PVAc and PVBAc wash primer precipitates dissolved immediately leaving a green powdery material (apparently  $\text{CrPO}_4$ ) and clear solutions. When the clear solutions are precipitated in water they yielded a white polymer. The PVBAc chromium precipitate is not completely soluble in

95% EtOH but neither is the PVBac resin itself. Bl, of course, does not dissolve, and in all cases was very similar in appearance to the remainder from the PVBac and PVAc precipitates after extraction with solvent.

The precipitate from PVP-WP does not completely dissolve in any organic solvent. A green swollen polymeric material remains while the solution is clear and colorless. On addition of the supernatant liquid to water a white polymer precipitates.

Treating the Cr-PVB-WP first with oxalic acid, and treating it then with organic solvent, changes the resin to a less soluble form. It is not clear whether this is a specific effect of oxalic acid, or a result of the Cr-removal. More experiments are under way.

In order to ascertain how much of the polyvinyl butyral could be removed from Cr-PVB-WP by ordinary solvents, the following experiment was conducted.

10.00 gms. of the complete wash primer was precipitated, the precipitate washed very well, torn up into small pieces, and shaken with 50 ml. of dioxane for 8 hours, the dioxane decanted and 50 ml. of more dioxane used for 16 hours further shaking. The solutions were combined, filtered by gravity, washed with 20 ml. of dioxane, and freeze dried. The recovered polymer was white and was saved for comparison with the original polyvinyl butyral XYHL by viscosity measurements.

In this recovery process, 0.90 gms. (not oven dried) were obtained while the residue weighed .44 gms. after vacuum drying at 55°C. This total can be accounted for approximately as: resin, 1.10 (.90 + .20) gms; Cr, .05 gms; phosphate (complexed or anionic) .09 gms.; waters of hydration (figuring 3 per Cr) .05 gms.; total 1.29 gms., or 82% of the resin dissolved.

3. The intrinsic viscosity of the extracted polymer in methyl ethyl ketone was found to be .38 cm<sup>3</sup>/gm as compared with .55 for the original XYHL polymer. The k' constants in the expansion

$$\eta_{sp/c} = [\eta] + k' [\eta]^2 c + \dots$$

for the extracted polymer and for XYHL, however, were very similar.

pH measurements were made on PVB-WP and the B1 blank, both added to a 10-fold excess of water (polymer precipitates). The pH from the PVB wash primer was 2.65 ± .05, and that from the B1 blank was 2.42 ± .05. This could be accounted for by the redistribution of protons over the PO<sub>4</sub><sup>3-</sup> ions which have been released by the complexing of Cr<sup>3+</sup> by the resin, but further studies will have to be made before the reaction can be clarified. Viscosity measurements of ethanol dilutions of PVB-WP prove in any case that the CR-resin complex is a strong polyelectrolyte, see Fig. 14. Electrophoretic experiments to determine the charge are under way.

DISCUSSION.

Again an appreciable part of our efforts was directed towards adsorption studies and it may, therefore, be appropriate to review the reasons for this emphasis in somewhat greater detail than was done in the discussion of the previous report (pp. 25-27).

It is true that for "good adhesion", and more so for a "good coating", more is required than mere adsorption. In many cases, those of so-called physical adhesion, adsorption is not even necessary. In true adhesion on smooth surfaces, adsorption certainly is the primary factor, but the conditions of wash primer coating are very different, and rather akin to the formation of a bond where there is considerable penetration, or solution, of surface and adhesive, and the boundary layer is more of the nature of a separate intervening phase than that of an adsorbed monolayer. However, notwithstanding these arguments, and just because of the complicated nature of the Vybond coating, we believe it to be most likely that adsorption in its various forms, including chemisorption, is of overriding importance.

The surfaces treated in practical applications are neither smooth nor clean and, apart from various contaminations, may be said to consist mainly of different iron, or generally metal, oxides of considerable depth, and include adsorbed oxygen. When treated with an alcoholic acid, some of these oxides will



be converted into salts, but in view of the relatively short times, low acidities and solubilities, this conversion will be limited in degree and will lead mostly to the formation of some oxy-salts. Most of the deposited salts will be chromium and zinc phosphates stemming from the action of the phosphoric acid on the pigment and the reduction of chromate to chromic ions by the alcohol. There will also be some electrolytic redistribution of ions due to local currents depending on the structure of the underlying metal and the state of passivation, and a similar redistribution of phosphate ions, but by and large the surface structure of the inorganic constituents along an imaginary cut perpendicular to the surface will be that of a gradual change from pure metal to oxides, basic salts and chromium or zinc phosphate.

This surface layer would afford a very good protection of the surface against further corrosion, were it not for the fact that the mentioned surface compounds are not sufficiently insoluble, tight or mechanically strong towards continued exposure to other aqueous salt solutions. As a result, even where these protective surface compounds are not liable to peel off because of poor cohesion and porous structure, their composition would become gradually altered into more soluble forms as a consequence of ion exchange mechanisms in an environment poorer in trivalent ions than the primary solution was. A progressive deterioration of corrosion protection will set in since, in the absence of agents which will insure highly oxidized states, a

more soluble surface layer means more ionization and local corrosive currents.

From this picture the part played by a hydroxyl containing resin with complexing properties like PVB clearly emerges. By forming mixed complexes or compounds in the pattern of basic salts such a resin will become tied to ionic compounds at any level where the solution penetrates, from the deepest oxide layer to the topmost chromium phosphate. The resin molecules will thus interweave with basic salts attached to the metal substrate, with individual salt molecules as well as with flakes, granules, or microcrystals of salts, and will thus act like a matrix or a cement that changes crumbly structures into tough coatings, much in the manner proteins act in bone and tooth structures, polycarbohydrates react with polyvalent ions or strong bases, or phenolics or polyesters behave towards incorporated fillers and in lamination.

Apart from this binding action, the resin will further fulfill an important function by reducing ion exchange. The hydroxy compounds of trivalent ions have a much lower solubility product than their phosphates, carbonates, lactates, etc. By participating in mixed salt-hydroxyl complexes, with or without chelate formation, the number of free ions will be greatly reduced with respect to those from pure phosphates under comparable conditions, with a subsequent stabilization of composition. It should be added that the solubility of the resin in

aqueous solution is itself vanishingly small, so that fixation of resin on a metal oxide surface by adsorption and evaporation from an alcoholic solution and subsequent exposure to water will lead to a coating as permanent as the resin structure itself.

From the above thesis, two main lines of research may be designed to elucidate the actual position: One is to study the resin-salt complexes and their stability, the other to investigate the adsorption of the resin to various oxide or salt surfaces. Both approaches are almost equivalent, the one emphasizing the combination in solution leading to insoluble compounds, the other stressing the magnitude of the forces and the amounts of resin actually tied to existing surfaces. The latter approach, being the more general and phenomenological study, promises to yield quicker, more direct results, while the study of the nature of the complexes will cast light on the nature of the binding forces and the type of adsorption or chemisorption involved. Consequently, we thought it advisable to follow both paths and to further broaden the approach and ease the interpretation of results by including such related resins as polyvinyl-acetate, polyvinyl alcohol, acetylated butyral, polyvinyl formal, etc.

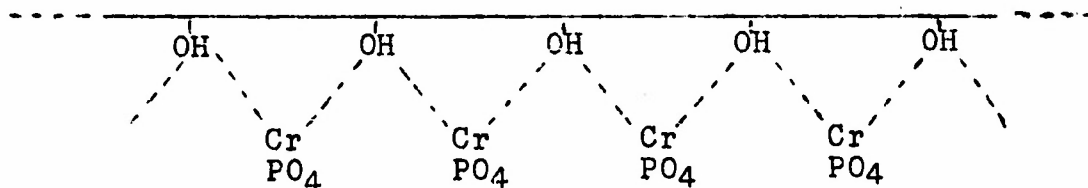
In this perspective the significance of our results will be more readily seen. The dependence of adsorption on molecular weight is of primary importance, as the general mechani-

cal strength of the coating will increase with molecular weight. The desirability of applying high molecular weight will therefore be only limited by practical consideration of manufacture and handling-viscosity. Similarly, the greater adsorption of high molecular weight from poorer solvents is of more than theoretical significance. It might be argued that this enhanced adsorption is of secondary importance, since the resin is affixed anyway by solvent evaporation and subsequent aqueous precipitation. While this is true, the distribution of the resin on the surface and between phosphate grains, etc., will vary greatly with strength of primary adsorption. The greater the latter, the more uniform will the resin be distributed and stay so, and the greater will be the thermodynamic and mechanical stability of the resin matrix-salt composite. In a similar way, the temperature of application will matter, and vary from solvent to solvent, in accordance with the thermodynamics of the solvent-solute system, as found by us. A more detailed discussion shall be postponed till we have as complete data for PVB as for PVAc, although the basic features observed with PVAc are likely to be true for the whole group of resins under consideration. In any case, once the PVB data are secured, especially those of original and of recovered samples, a structural comparison will become fruitful.

The physical structure of the adsorbed layer will further be illuminated by the degree of obedience of the adsorption isotherm to models of adsorption. In preliminary attempts,

the data of the first set of experiments (analysis by infra-red) appear to fit better a Freundlich type isotherm, while those of the second set can to a degree be fitted by a Langmuir isotherm. Either the different methods or the different origin of the samples may be held responsible for this divergence; if the latter explanation were found to be true we would have good reasons to attribute the differences to the degrees of branching of the two samples: those of Set 1 are more linear molecules from polymerization to low conversion, those of Set 2 are high conversion samples and likely to have appreciable branching, probably in excess of that apparent on XYHL-Ac and XYSG-Ac (see previous report). A detailed discussion shall be postponed till more data are available.

With respect to wash primer formation, we have seen that all chromate becomes reduced to  $\text{Cr}^{3+}$ -ions, and that the resulting  $\text{CrPO}_4$  is completely complexed by the resin. Comparing the quantities, the molar ratios of  $\text{CrO}_3:\text{H}_3\text{PO}_4:\text{PVB}(-\text{unit})$  is approximately 0.5:1:10, but in equivalents, and counting the hydroxyl groups of the resin only (including those due to the hydrolysis by the phosphoric acid), the ratio becomes rather 1.5:3:4. Even so, approximately one half of the phosphoric acid remains as acid (one proton disappears for each reduced valency on the chromium) and all the  $\text{CrPO}_4$  can be tied to the resin in a stoichiometric ratio depicted by structures like:



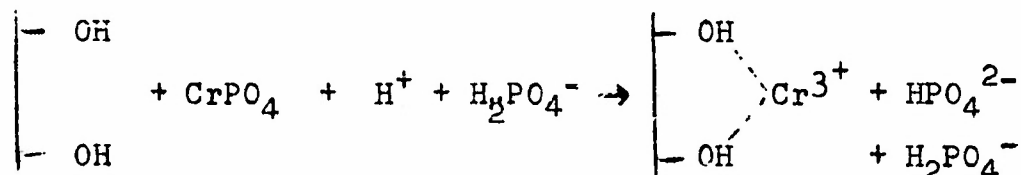
In these structures, which can be visualized intra- or inter-molecularly, the  $\text{CrPO}_4$  takes the place of the acetal aldehyde. Where the resin is soluble, as in alcohol, it will solubilize the  $\text{CrPO}_4$ ; i.e.  $\text{CrPO}_4$  can be considered adsorbed on resin molecules. Where the resin is insoluble, as in water, the  $\text{Cr-OH-resin}$  bonds will be sufficiently weakened by competition with  $\text{H}_2\text{O}$  to permit the formation of amorphous  $\text{CrPO}_4$ , but not enough to separate the resin entirely from this sediment on which it can now be considered adsorbed.

It fits into this picture that no crystalline structure could be found in the  $\text{CrPO}_4$ -resin precipitates by X-rays, but it has also to be pointed out that neither a brief X-ray study of our own, nor a search through the literature, revealed any evidence of crystallinity for  $\text{CrPO}_4$  by itself. In view of the well known tendency of chromium compounds to hydrate and to polymerize, it may well be that  $\text{CrPO}_4 \cdot n\text{H}_2\text{O}$ , as so many vinyl polymers, forms so many isomeric polymers as to preclude crystallization. PVB may be expected to fit molecularly very well into such a pattern and to become strongly adsorbed, or to be present in solid solutions.

Some further light is thrown on the  $\text{Cr-PVB}$  complex structure by our observations with respect to pH-changes, effect

of OH-group masking, chelation, solvent extraction, and polyelectrolyte nature. When the  $\text{CrPO}_4$  reacts with the resin, the  $\text{Cr}^{3+}$ -ions, while not losing their charges, become reduced in their activity by the process of complexing. This is tantamount to a greater solubility of  $\text{CrPO}_4$  in that the  $\text{Cr}^{3+}$ -ions are being held by the resin while the phosphate-ions dissociate; the latter represent thereby the counter-ions of the polysalt constituted by the resin Cr-complex phosphate.

The  $\text{PO}_4^{3-}$ -ions thus returned to the solution will equilibrate with the protons of the excess phosphoric acid; at  $\text{pH} \leq 8$  the concentration of trivalent phosphoric acid ions is very small, so that  $\text{PO}_4^{3-}$  will act as a base. Schematically, the reaction can be formulated as:



so that the pH in the presence of a resin which complexes  $\text{Cr}^{3+}$  will be higher.

It will be seen that such a reaction scheme immediately accounts for the observed facts of pH-shift, polyelectrolyte behavior, necessity of OH- groups on the resin for Vybond-type complexing, solubilization of  $\text{CrPO}_4$ , as well as for the sometimes asserted excess of  $\text{PO}_4$  belonging to the complexed resin; it also renders unnecessary the assumption of Cr-ions of valency higher than 3 being complexed.

The question may be raised, why the alcohol which is present in such large molar excess, does not participate with its OH-groups in the complexing, or compete with the resins, while water does, as postulated below. The reasons for this comparative inactivity of the alcohol are the same which cause the differences in dielectric constant, or in viscosity, between alcohol and water: the greater effective dipole moment of the latter and greater tendency to hydrogen bonding.

The picture outlined to this point refers to the solution state of  $\text{CrPO}_4$  and resin in a recently prepared chromium wash primer. During the practical application, however, the wash primer is applied to a surface and dried by alcohol evaporation. During our precipitation experiments, water is added and precipitates the resin and with it the chromium. These two processes are seemingly very different and at a later stage we plan to investigate the drying process. At the same time we believe, as the further discussion will endeavour to show, that actually the differences of what happens in these two cases is more quantitative than in kind.

In the drying process, the formation of an organo-gel is soon interrupted by the rising concentration of water present in appreciable quantities as shown on p. 12, which will co-precipitate the resin +  $\text{CrPO}_4$ . The resin will precipitate as an amorphous aggregate with OH-groups turned outwards as the mixture becomes a non-solvent; at the same time the water



molecules will compete with the OH-groups of the resins sufficiently strongly as to disengage the bulk of the  $\text{CrPO}_4$  from the resin leaving an intricate mixture of mutually adsorbed aggregates. On further loss of solvent and water other processes will take place such as more and more cross-linking of the resin, and dehydration of the  $\text{CrPO}_4$ . Actually, the same processes, except for those accompanying extensive dehydration, will occur on aqueous precipitation.

Apart from the arguments used before, these inferences are based on our, as yet incomplete, observations during extraction experiments. The complete removal by solvents of the acetylated resins proves the existence of a special function of the OH-groups, in the form of some chemisorption (complexing) to the  $\text{CrPO}_4$  precipitate. Solvents, which compete with  $\text{CrPO}_4$  for the resin, are only partly successful in extracting the PVB, failing to extract molecules for which the Cr-ions act as cross-linking agents. Good chelating agents, on the other hand, compete successfully with the resin for the Cr-ions by being able to form stronger, and possibly covalent, bonds. Weaker chelating agents rather replace the phosphate ions and associate with the Cr-ions on the resin.

These considerations, incidentally, present a departure from an earlier speculation according to which two or more types of reactive groups in the resin might be involved in complexing Cr-ions, thinking of  $-\text{COOH}$  or the acetal groups (see

previous report, p.24). Our present data argue rather against anything but weak adsorption of acetal and acetate groups on  $\text{CrPO}_4$ , and we presume now that some cross-linking has taken place in the resin as a consequence of the adsorption to  $\text{CrPO}_4$ .

It is not clear why the resin should have become less soluble after the Cr-ions have been extracted from the precipitate. This may be indicative of the existence of some covalent bonds between Cr-ions and resin which after the removal of these ions join inter-molecularly. However, we believe this to be unlikely and rather think that in the presence of oxalic acid esterification and etherification takes place analogous with the aging and dehydration reactions going on in the resin on drying (in the presence of free phosphoric acid). Similarly, we do not believe that the lower viscosity of the resin extracted from the wash primer precipitate as compared with the original viscosity of the PVB used is due to adsorptive fractionation, but rather that it is a result of the destruction of aldehyde cross-links (present in the original PVB) during the moderate acetal hydrolysis which takes place in the course of the wash primer formation (see also the previous report, Table V).

Summing up, we believe to have shown that the picture as outlined is capable of explaining all observed features, and even some less explored ones like the effect of the wash primer on other metals or even on such diverse non-metallic surfaces as glass, other vinyl resins if aged, or wood. Many

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features had to be left rather vague for lack of knowledge, but may become clarified as the work progresses.

FIGURE - I      ADSORPTION ISOTHERMS FOR POLYVINYL ACETATE  
 IN  $\text{CCl}_4$  ON TO Fe AT  $30.4^\circ\text{C}$

SAMPLES: 1 - XYHL  
 2 - XYSG  
 3 - #6  
 4 - #4  
 5 - #2

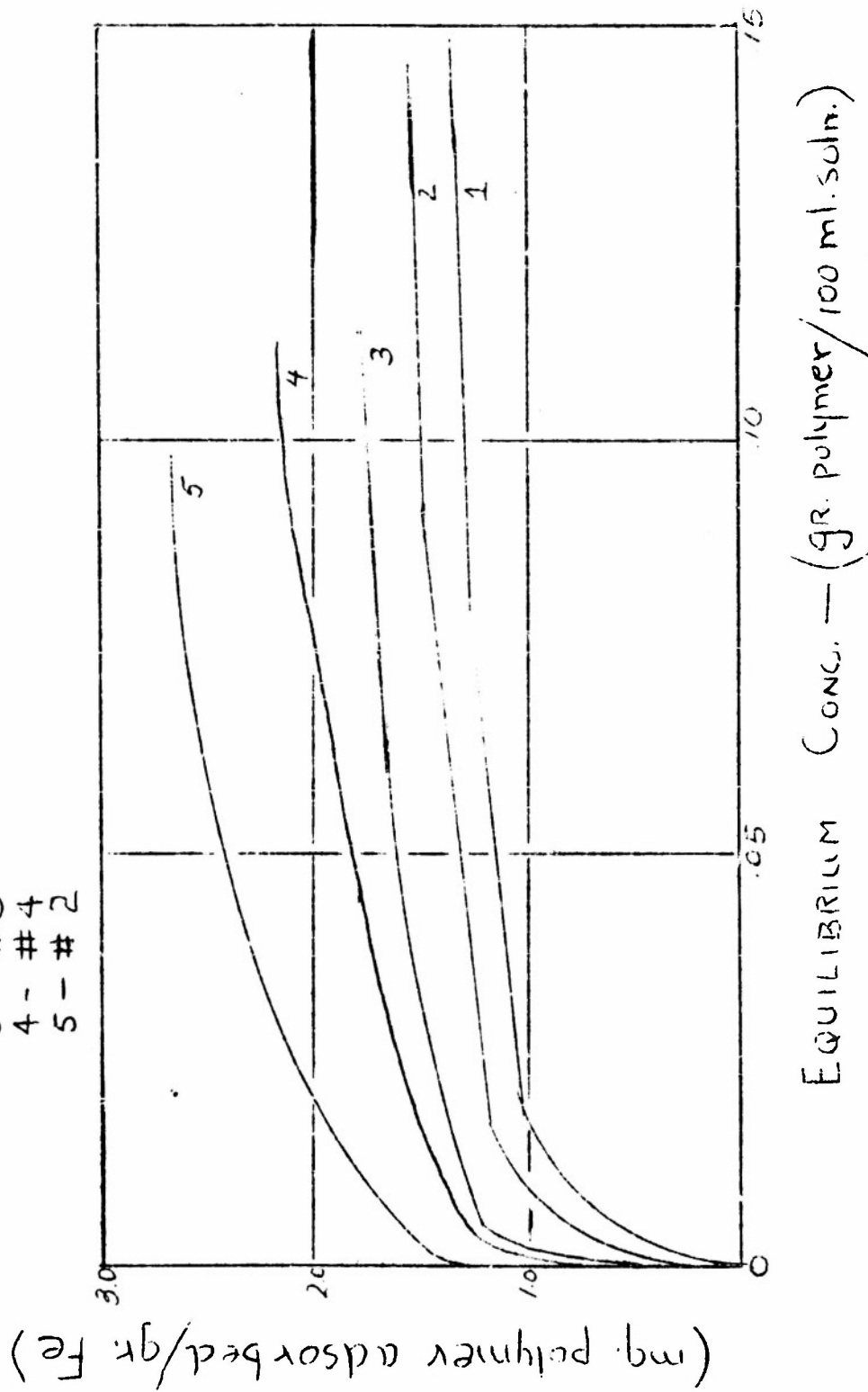


FIGURE - II CALIBRATION CURVE FOR POLYVINYL ACETATE  
IN  $(CH_2)_2Cl_2$

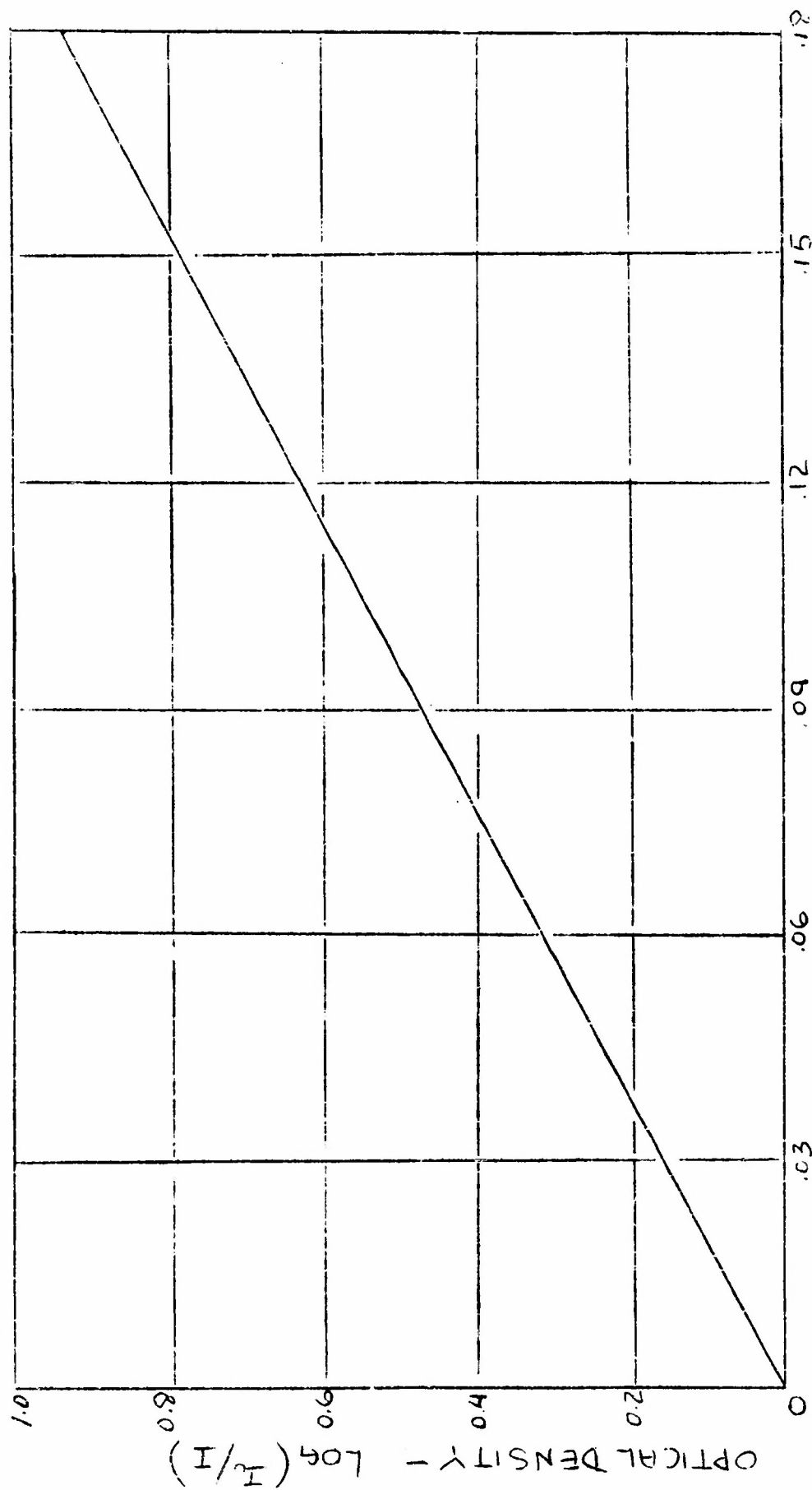
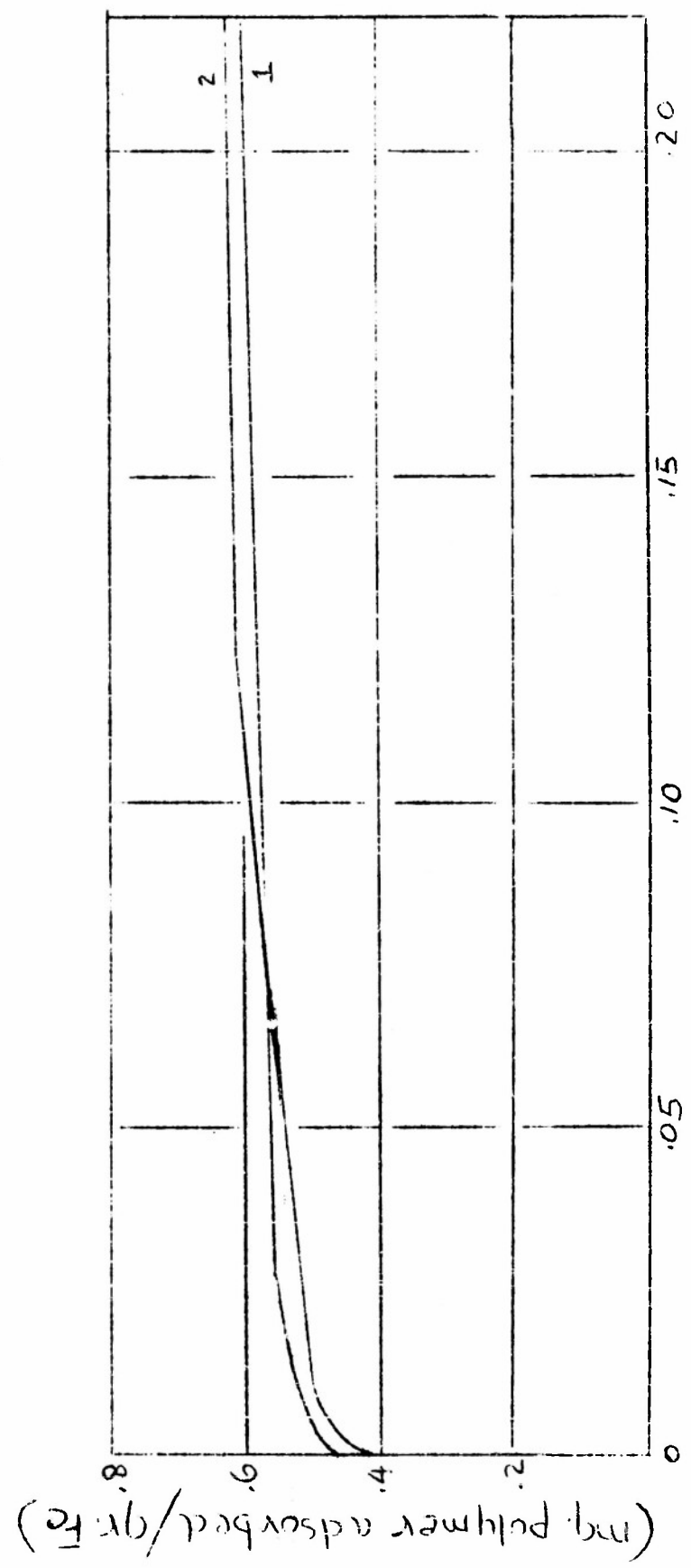


FIGURE - III

ADSORPTION ISOTHERMS FOR POLYVINYL ACETATE - #2

IN  $(CH_2)_2Cl_2$  ON TO Fe AT  $30.4^\circ$  AND  $51.0^\circ C$

SAMPLES: 1 -  $30.4^\circ C$   
2 -  $51.0^\circ C$



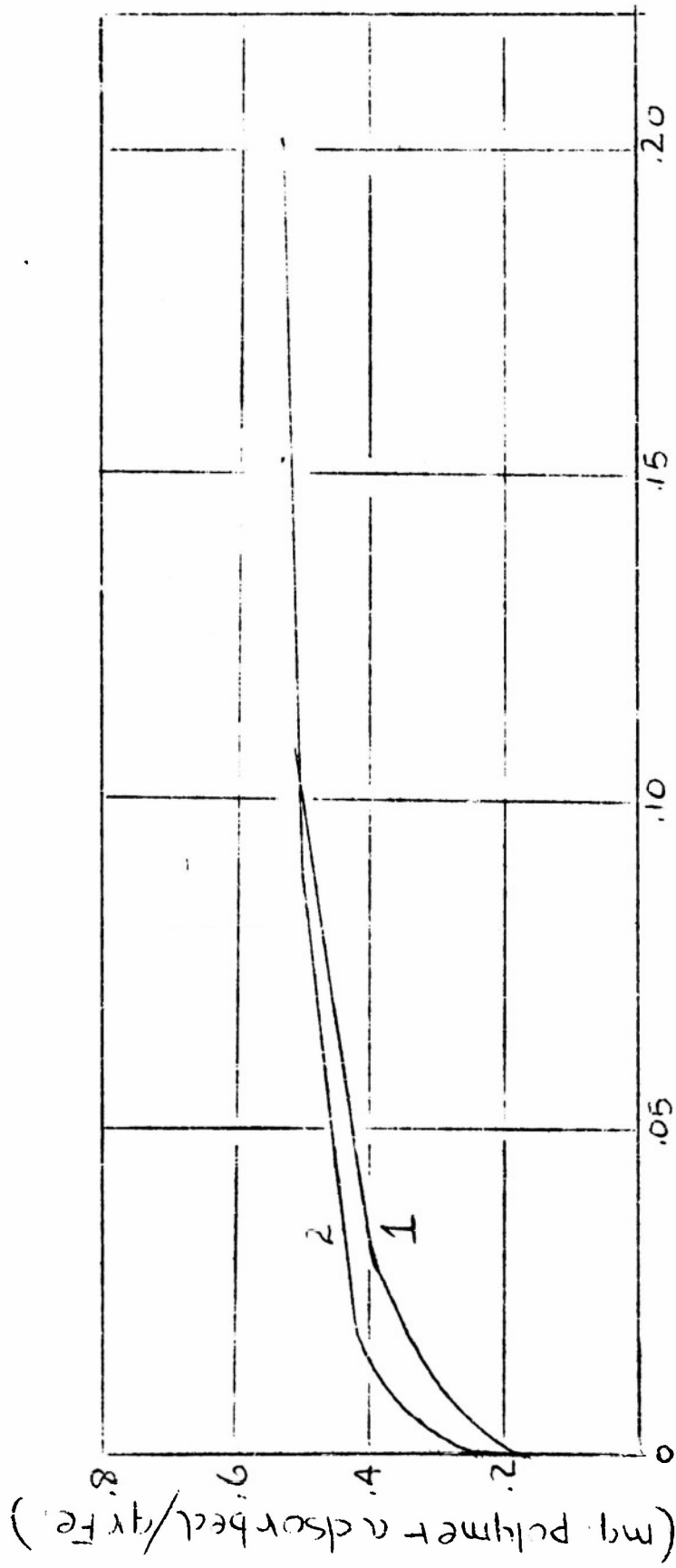
EQUILIBRIUM CONC. — (gr. polymer / 100 ml. soln.)

# FIGURE-IV ADSORPTION ISOTHERMS FOR POLYVINYL

ACETATE IN  $(CH_2)_2Cl_2$  ON TO Fe

SAMPLES: 1- XYSIG-30°C

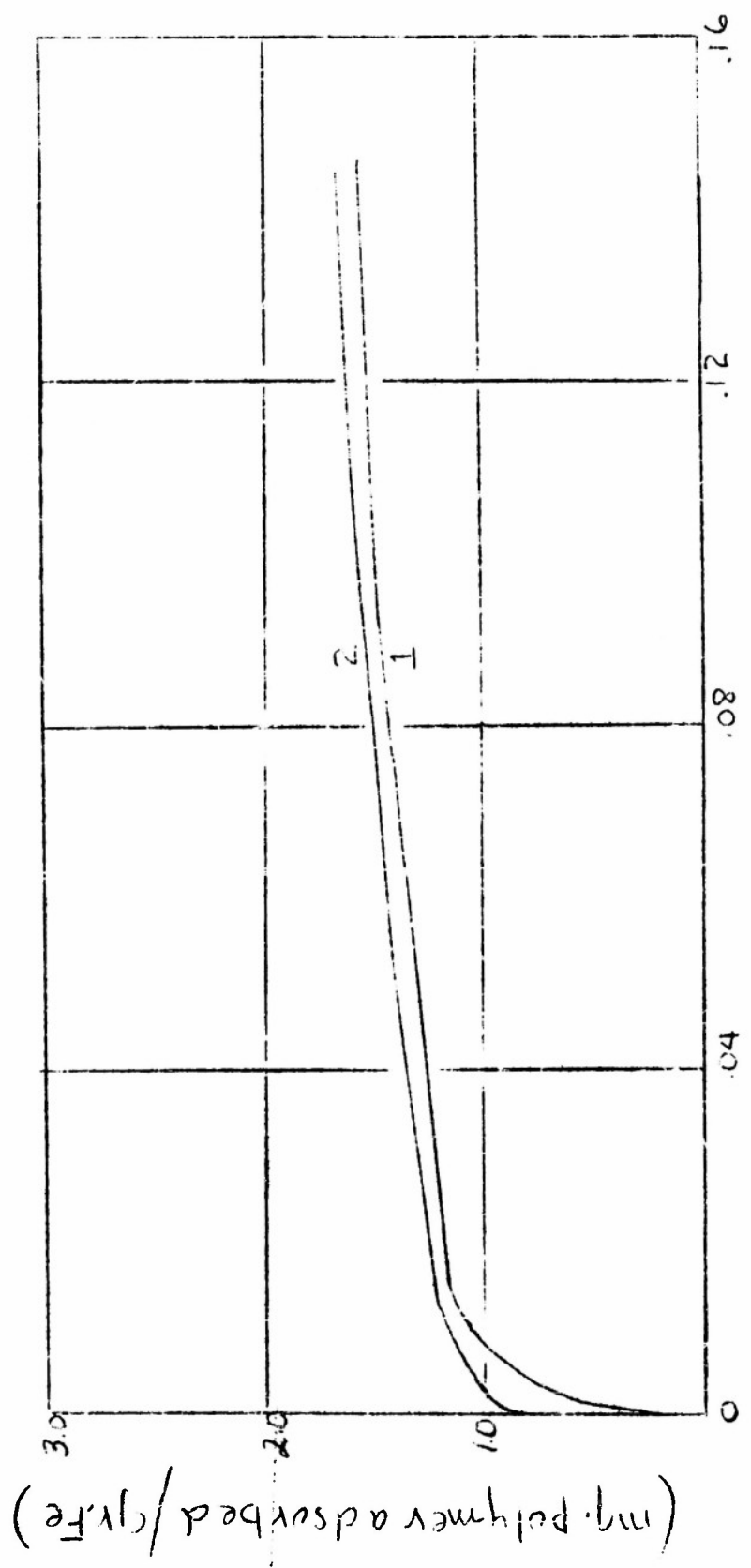
2- XYHL-50°C



EQUILIBRIUM CONC. - (gr. polymer/100ml. soln.)

FIGURE - V      ADSORPTION ISOTHERMS FOR POLYVINYL  
ACETATE IN CCl<sub>4</sub> ON Fe

SAMPLES: 1 - XYSG - 48.5°C  
              2 - XYSG - 30.4°C



EQUILIBRIUM CONC. ~ (gr. polymer / 100 ml. soln.)



FIGURE - VI

THE EFFECT OF MOLECULAR

WEIGHT ON ADSORPTION

SAMPLES. A -  $137.4 \times 10^3$   
 B -  $430.5 \times 10^3$   
 C -  $1,738 \times 10^3$

ADSORBENT - SILICA

SOLVENT - TOLUENE

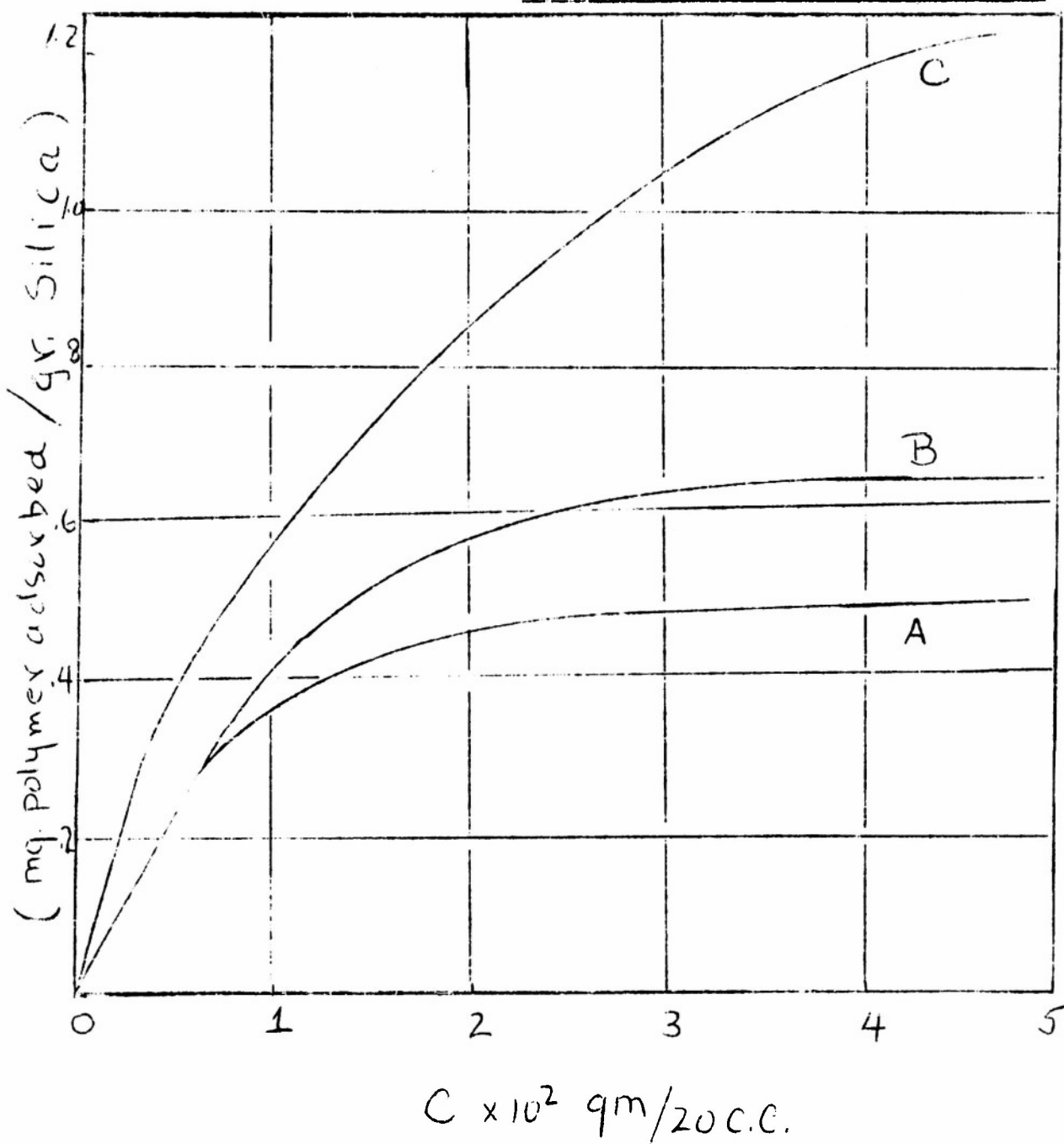
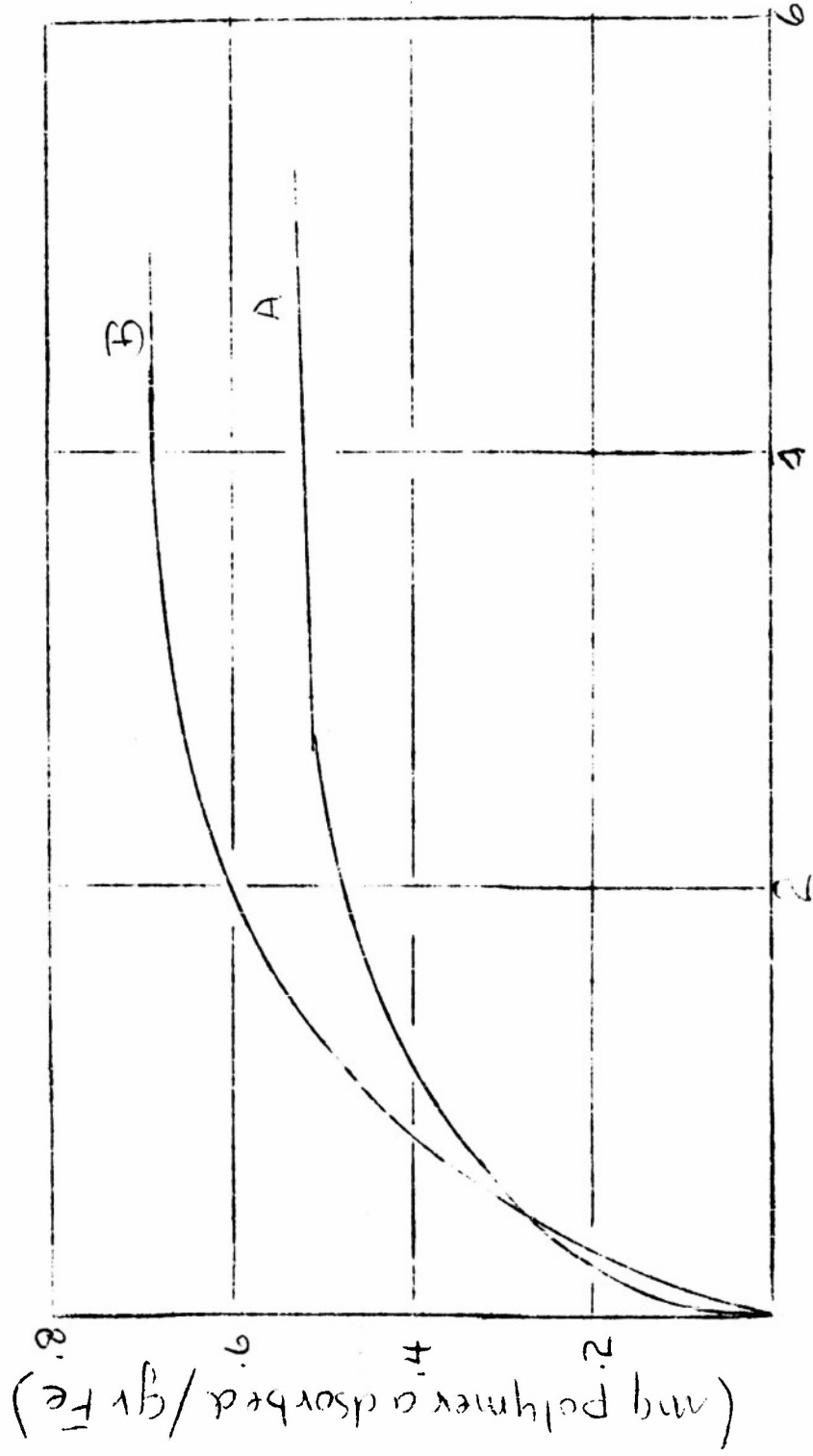


FIGURE - VII

THE EFFECT OF MOLECULAR WEIGHT ON ADSORPTION

ADSORBENT - Fe

SOLVENT - TOLUENE



$C \times 10^2 \text{ gr/20cc}$

FIGURE - VIII THE EFFECT OF MOLECULAR WEIGHT ON

ADSORPTION

ADSORBENT - SILICA  
SOLVENT - METHYL ETHYL KETONE

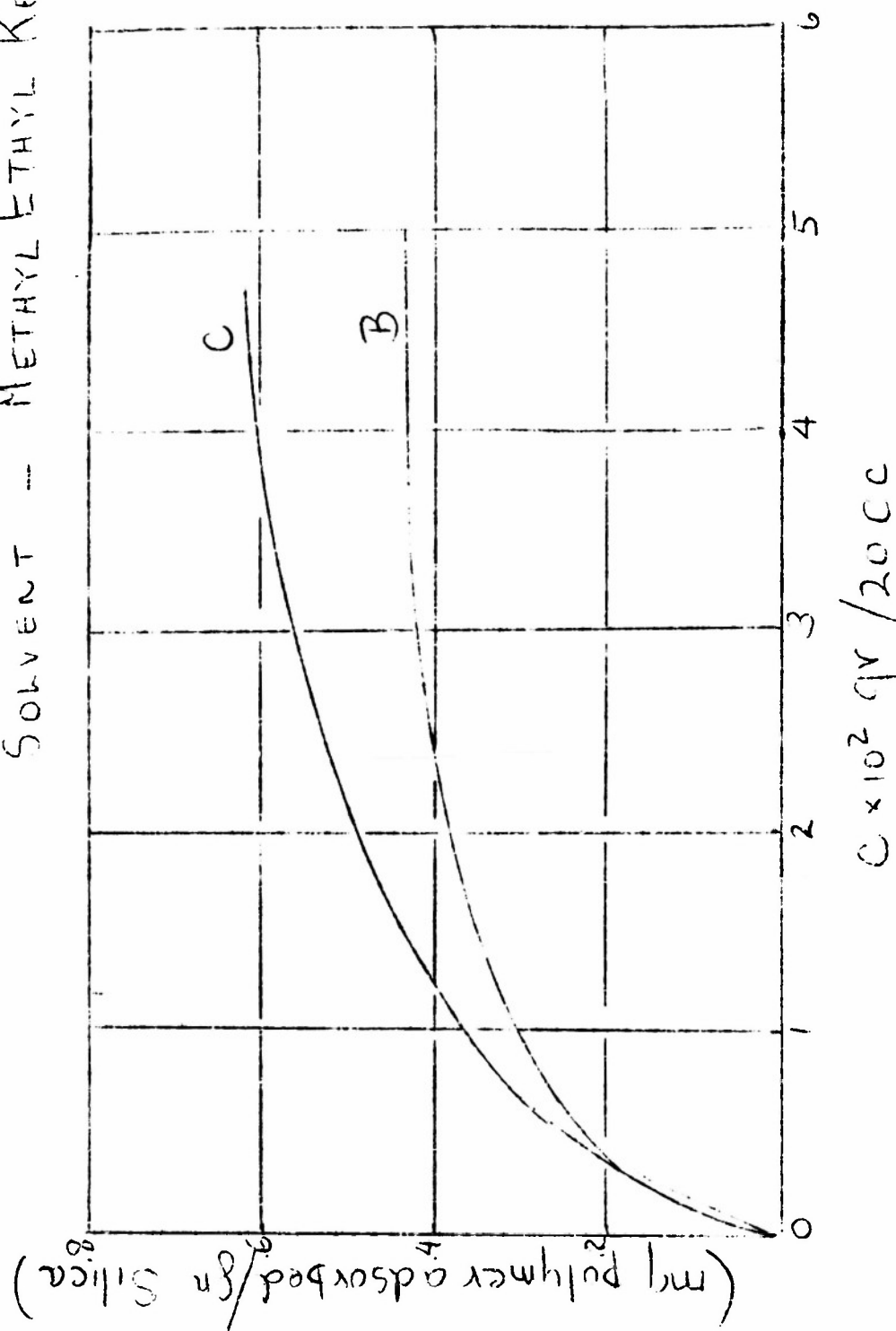
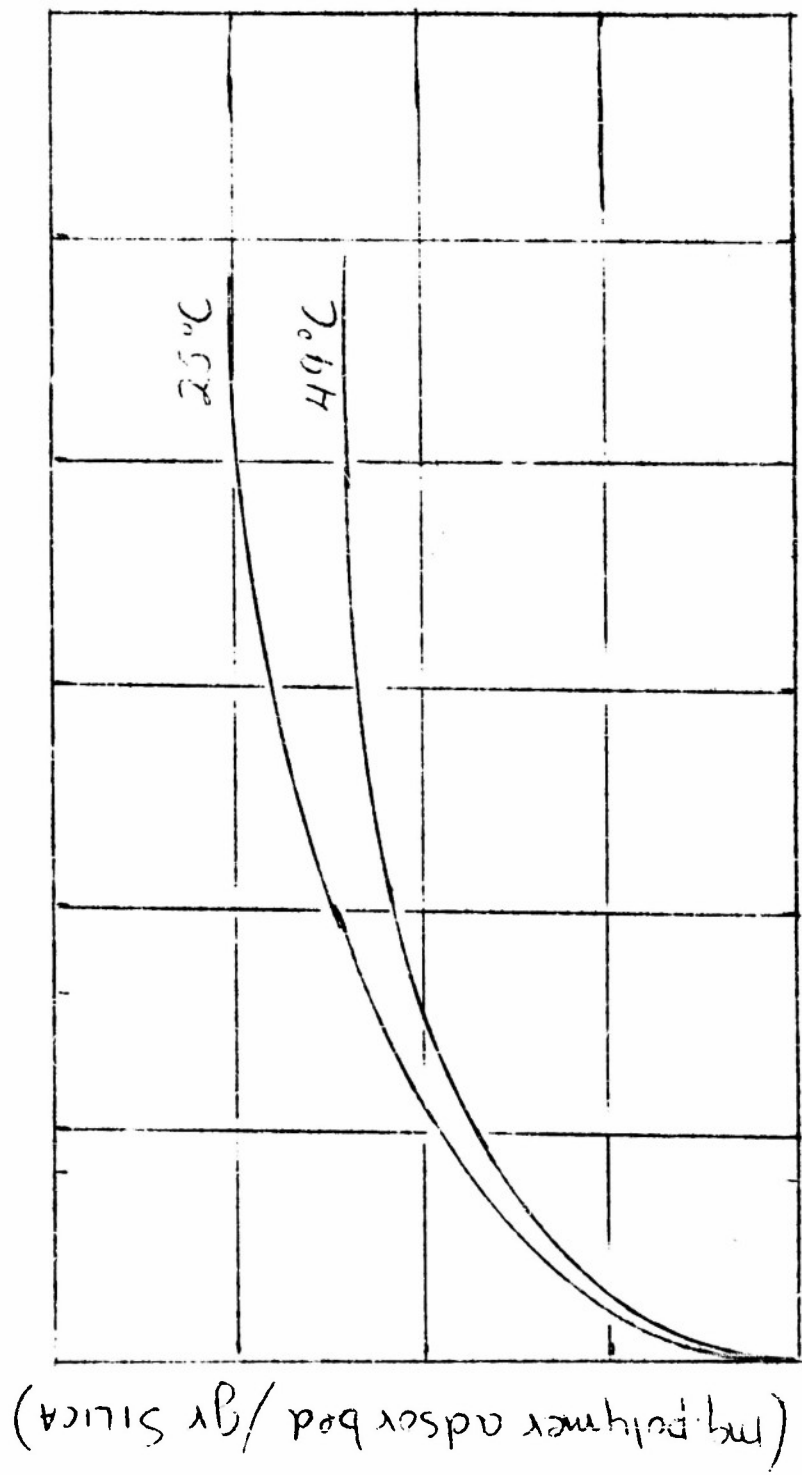


FIGURE - IX

THE EFFECT OF TEMPERATURE ON ADSORPTION

ADSORBENT - SILICA

SOLVENT - METHYL ETHYL KETONE



( $C \times 10^2$  gr / 100 cc)

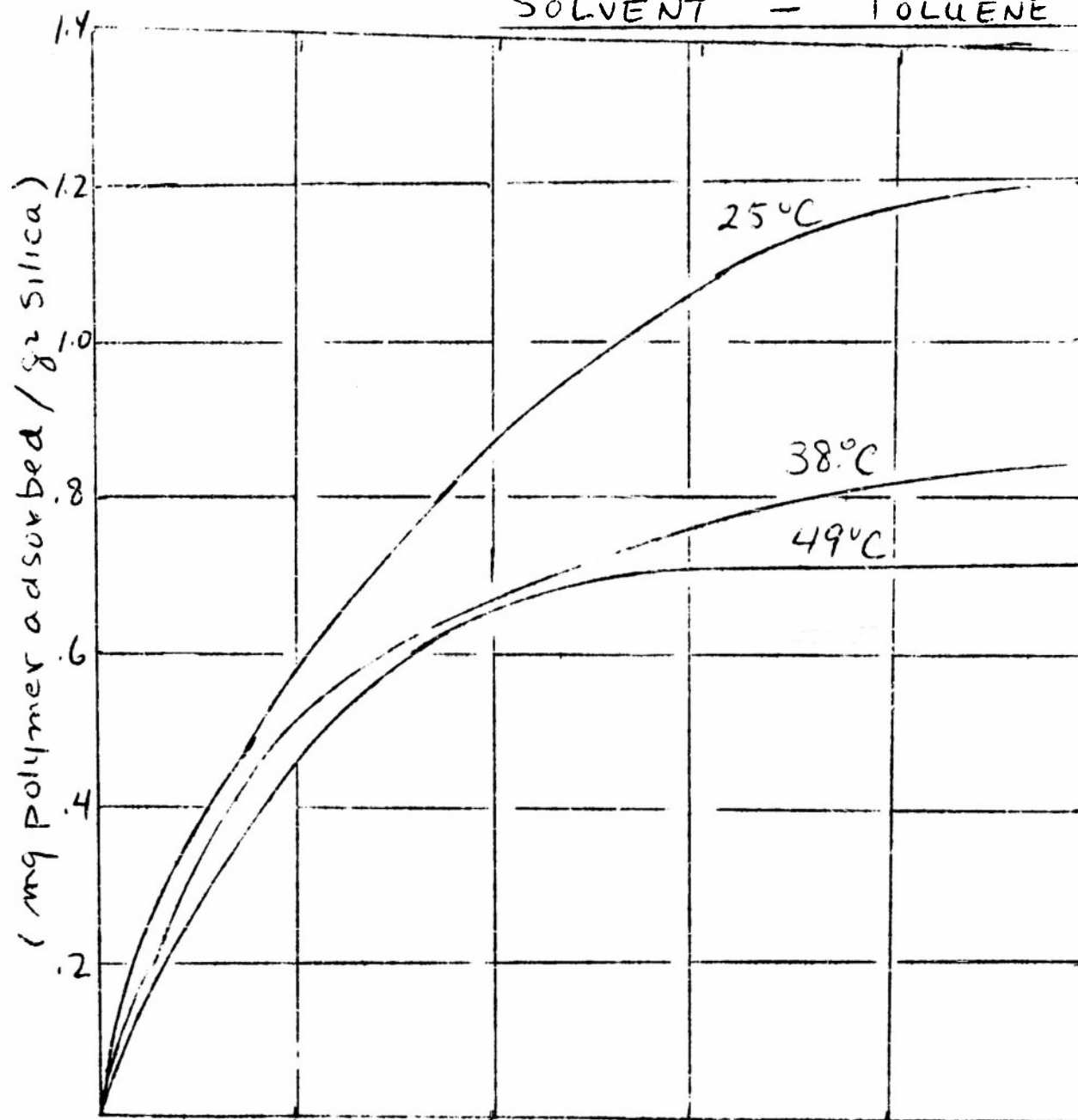
FIGURE - X

VARIATION OF ADSORPTION

WITH TEMPERATURE

ADSORBENT - SILICA

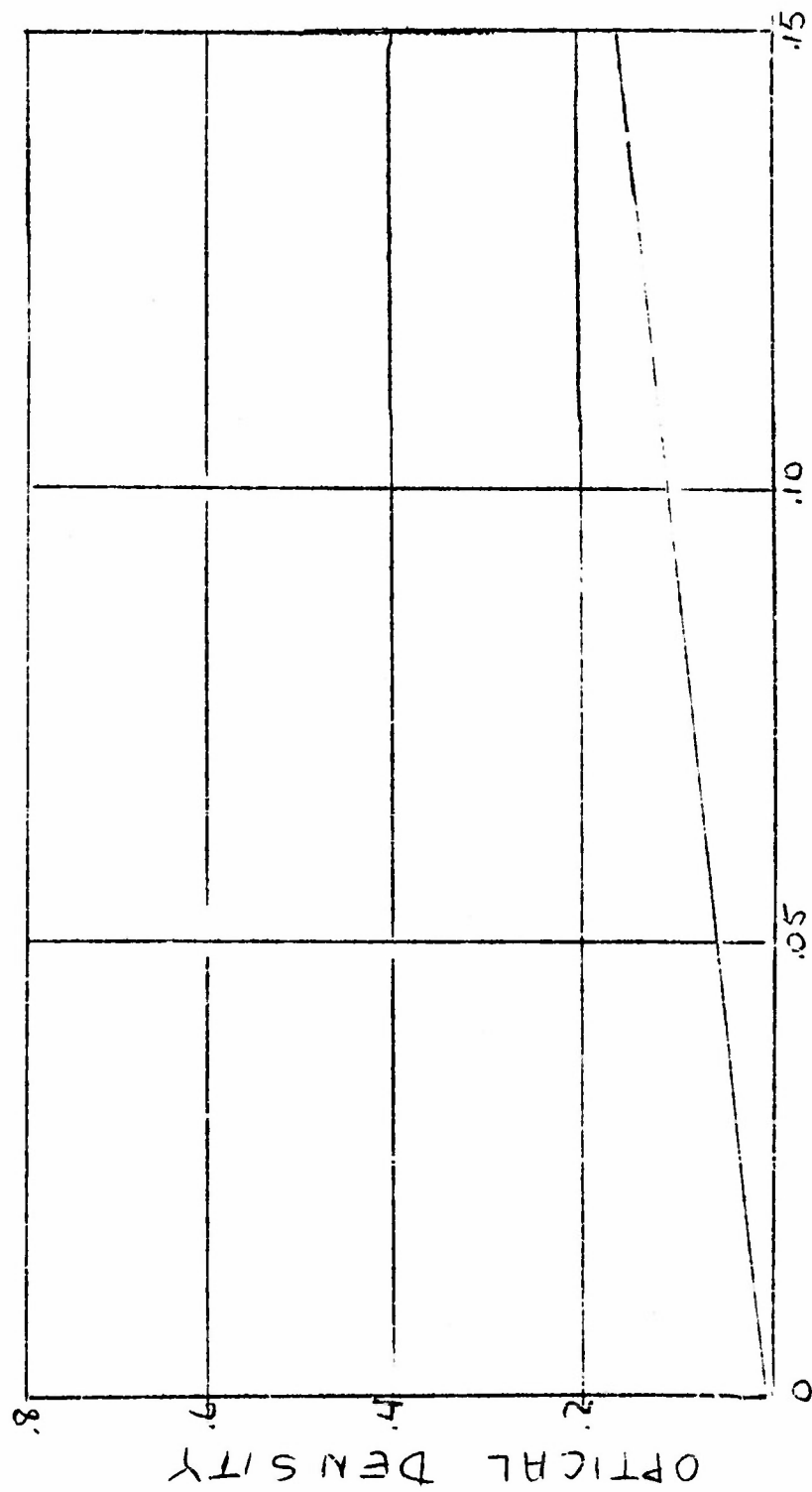
SOLVENT - TOLUENE



$C \times 10^2 \text{ g/l}$

FIGURE - XI      CALIBRATION CURVE FOR POLYVINYL

BUTYRAL IN  $(CH_2)_2Cl_2$



Concentration in (gr polymer / 100ml soln.)

FIGURE - XII

TIME OF SHAKING VS. AMOUNT OF

POLYMER ADSORBED

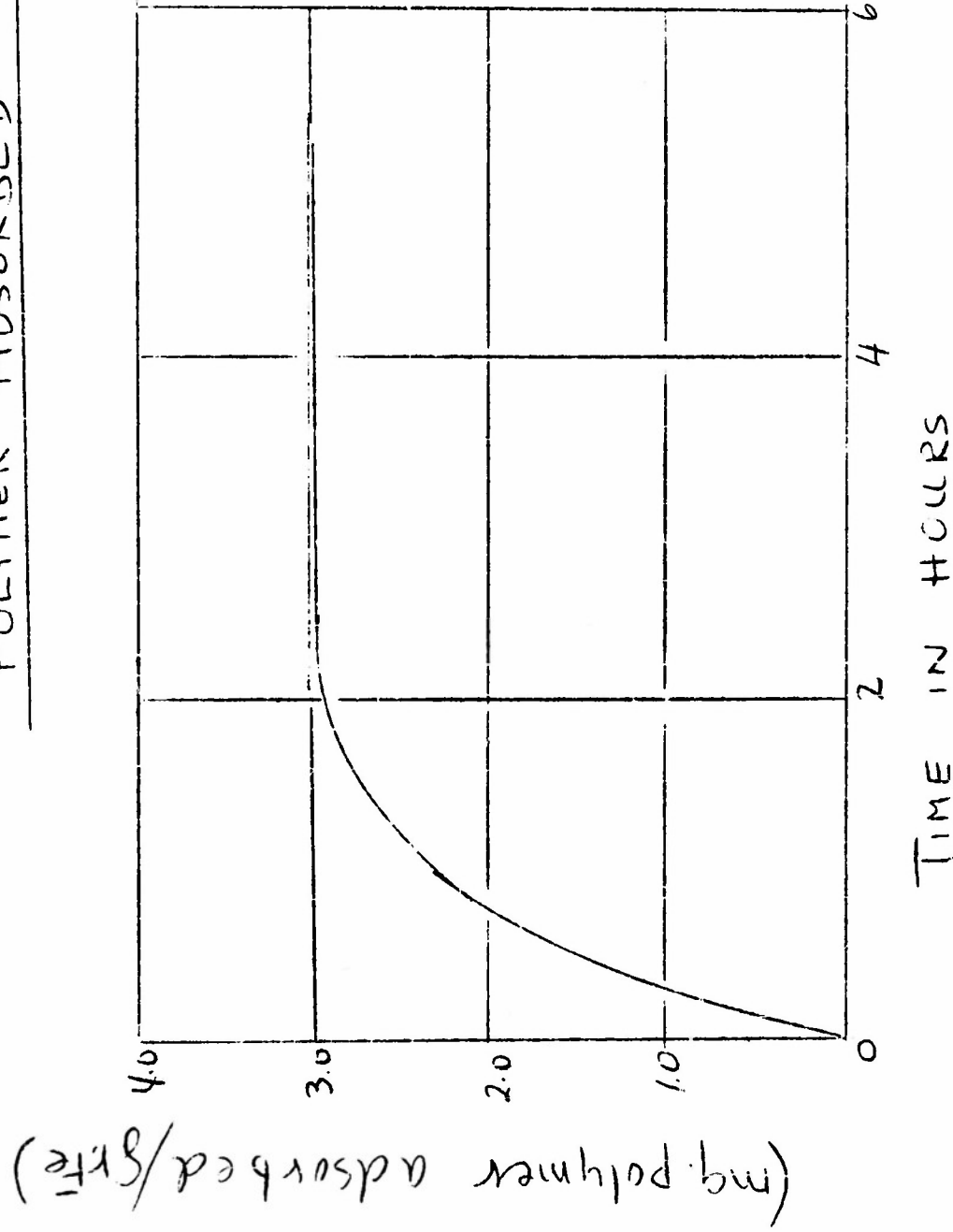


FIGURE - XIII

ADSORPTION ISOTHERMS FOR

POLYVINYL BUTYRAL FROM  $(CH_2)Cl_2$

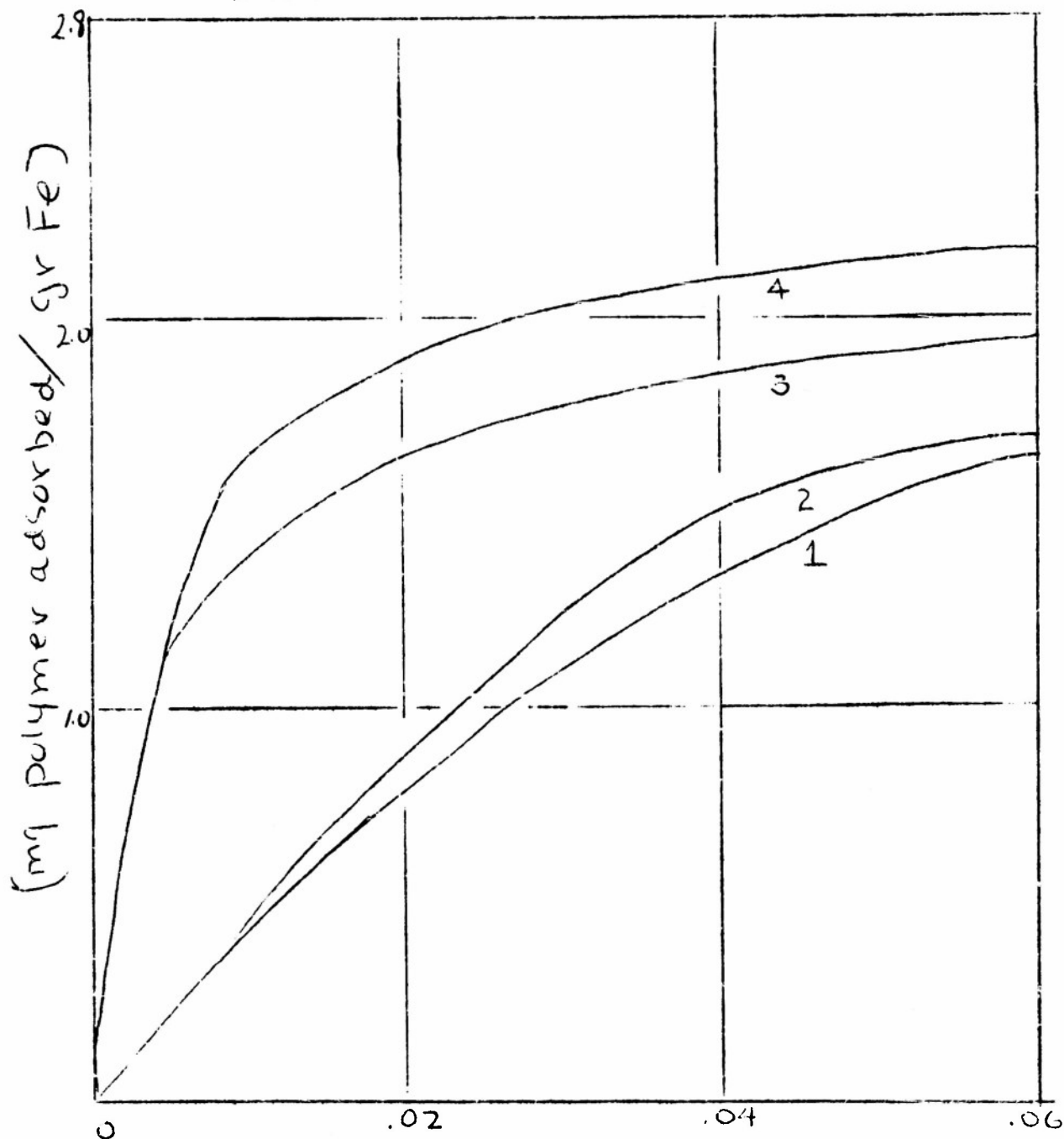
ON TO Fe

SAMPLES: 1 - XYSG - 50°C

2 - XYHL - 50°C

3 - XYHL - 30°C

4 - XYSG - 30°C



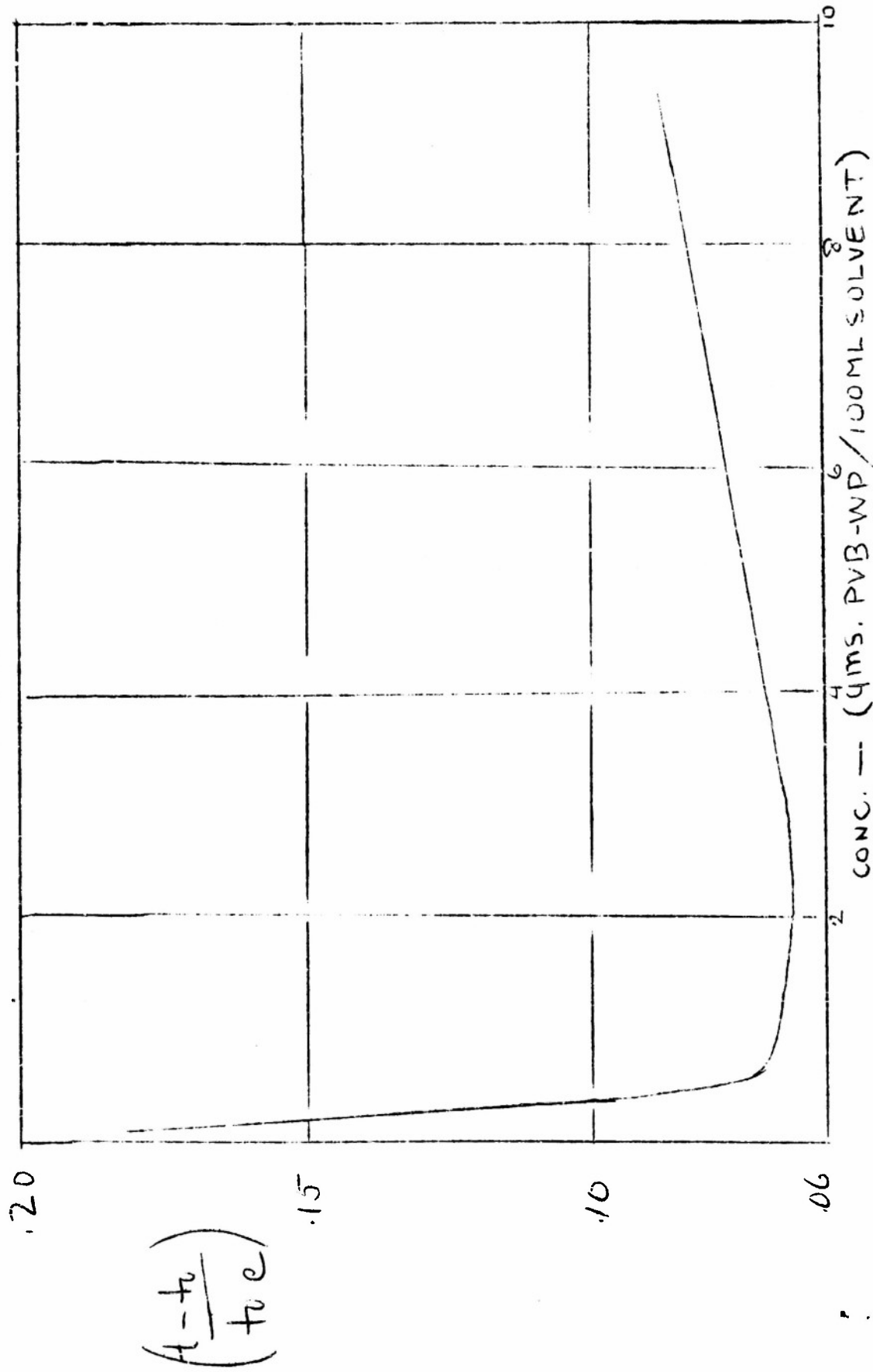
EQUILIBRIUM CONC - (gr polymer / 100 ml soln.)



FIGURE - XIV

VISCOSITY OF PVB-WP IN 94% ETHANOL

AT 24.7°C



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